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**Notes:**

1. Untranslatable words are replaced with asterisks (\* \*\*).
2. Texts in the figures are not translated and shown as is.

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1] A separator for cells which is a nonwoven fabric which makes composition textiles one kind or two kinds or more of polyolefin fibers, and is characterized by ion exchange nature grains coming to anchor by at least some resinous principles of a fiber surface of composition textiles.

[Claim 2] The separator for cells according to claim 1, wherein at least one kind of polyolefin fiber is a bicomponent fiber which uses one ingredient as an ethylene-vinyl alcohol copolymer.

[Claim 3] The separator for cells according to claim 1, wherein at least one kind of polyolefin fiber is a bicomponent fiber which uses one ingredient as high density polyethylene.

[Claim 4] The separator for cells according to claim 1 characterized by ion exchange nature grains filling a relation of  $P_{min} \leq D \leq P_{ave}$  when an average pore size of  $D$  and a nonwoven fabric is set to  $P_{ave}$  and the minimum aperture is set to  $P_{min}$  for mean particle diameter of ion exchange nature grains.

[Claim 5] The separator for cells according to claim 1 or 4, wherein ion exchange nature grains anchor two to 60 weight % in a nonwoven fabric.

[Claim 6] A separator for cells given in either of the Claims 1, 4 and 5, wherein ion exchange nature grains are zirconium system grains which introduced a sulfonic group.

[Claim 7] A cell incorporating the separator for cells according to any one of claims 1 to 6.

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**[Detailed Description of the Invention]**

[0001]

[Field of the Invention] This invention relates to the cell using the suitable separator for cells and this for alkaline batteries, such as a nickel cadmium battery, a nickel zinc carbon cell, and

a nickel-hydrogen battery.

[0002]

[Description of the Prior Art] Usually, although the nonwoven fabric which mainly consists of nylon or polypropylene fiber is used as a separator for cells, since the nonwoven fabric which consists of nylon fibers is inferior to alkali resistance, the nonwoven fabric which consists of polyolefin fibers, such as polypropylene, is used preferably. However, the nonwoven fabric which consists of polyolefin fibers is hydrophobicity, and since it is inferior to a wettability when it uses for a battery separator, the method of carrying out hydrophilization treatment of the nonwoven fabric which consists of polyolefin fibers is examined. As the hydrophilization treatment method, sulfonation treatment, fluorination treatment, graft-polymerization treatment of a vinyl monomer, Or the separator for cells which performed surface treatment treatment of a corona, plasma treatment, etc., or the separator for cells which anchored the grains which use binder resin for a nonwoven fabric like JP,H9-330694,A, and have hydrophilic performance is proposed.

[0003]

[Problem to be solved by the invention] However, there are the following problems in the above-mentioned separator for cells. For example, in the case of the former, sulfonation treatment, fluorination treatment, and graft-polymerization treatment of a vinyl monomer have a complicated disposal method, and it is in the tendency it to not only to become a cost overrun, but for there to be also environmental problems, such as waste fluid, and they to be kept at arm's length. In the case of a corona or plasma treatment, discharge energy is not fully transmitted to the inside of a nonwoven fabric, but the hydrophilic performance inside a nonwoven fabric falls, and the hydrophilicity under the pressurization and decompression at the time of charge and discharge is insufficient.

[0004] In JP,H9-330694,A, since it impregnates with a nonwoven fabric and the binder resin which dissolved in the organic solvent is dried, being not only bad but productivity is not good environmentally. Since a polyolefin fiber is exposed to an organic solvent, there is a danger that textiles hardness will deteriorate. And since comparatively a lot of binder resin between the composition textiles of a nonwoven fabric permeates and covers a fiber surface, the opening of the separator for cells obtained of a nonwoven fabric decreases, and it is inferior to the solution retention of an electrolyte. This invention is made in view of the above-mentioned problem, and is a thing.

The purpose is to provide the cell excellent in the separator for cells and a battery characteristic excellent in the solution retention of an electrolyte.

[0005]

[Means for solving problem] The separator for cells of this invention is a nonwoven fabric

which makes composition textiles one kind or two kinds or more of polyolefin fibers, and ion exchange nature grains come to anchor by at least some resinous principles of the fiber surface of composition textiles. By taking this composition, productivity is good and the separator for cells excellent in the solution retention of an electrolyte is obtained.

[0006]As for said at least one kind of polyolefin fiber, it is desirable that it is a bicomponent fiber which uses one ingredient as an ethylene-vinyl alcohol copolymer, and it is desirable that it is a bicomponent fiber which uses one ingredient as high density polyethylene.

[0007]In ion exchange nature grains, when the average pore size of  $D$  and a nonwoven fabric is set to  $P_{ave}$  and the minimum aperture is set to  $P_{min}$  for the mean particle diameter of ion exchange nature grains, it is desirable to fill the relation of  $P_{min} \leq D \leq P_{ave}$ . As for ion exchange nature grains, it is desirable to anchor two to 60 weight % in a nonwoven fabric, and, as for ion exchange nature grains, it is still more desirable that they are the zirconium system grains which introduced the sulfonic group.

[0008]The cell incorporating said separator for cells has low internal pressure, and is suitable for the alkaline batteries excellent in battery characteristics, such as a core life and a capacity maintenance rate, such as a nickel cadmium battery, a nickel zinc carbon cell, and a nickel-hydrogen battery. Hereafter, the contents of this invention are explained concretely.

[0009]

[Mode for carrying out the invention]The separator for cells of this invention has a nonwoven fabric form which makes composition textiles one kind or two kinds or more of polyolefin fibers. The rate of occupying to the nonwoven fabric of a polyolefin fiber used for this invention is 80 weight % or more, and is 90 weight % or more more preferably. [ as polyolefin system resin which constitutes said textiles ] Polyolefine system polymers, such as polyethylene, polypropylene, the polybutene 1, the poly (4-methylpentene-1) 1, and an ethylene-vinyl alcohol copolymer, or the copolymer of those is mentioned, As a textiles form, a single fiber, a concentric circle or the sheath-core type bicomponent fiber of eccentricity, a parallel type bicomponent fiber, the fiber blend with which it comes to mix two or more kinds of said materials, a sea-island type bicomponent fiber, or an assembled-die bicomponent fiber may be mentioned, and sectional shape may also be any, such as circular and a variant.

[0010]And among said polyolefin fibers, as for at least one kind of polyolefin fiber, it is preferred that it is a bicomponent fiber which makes one ingredient the polymer which has adhesion ability with dry heat or wet heat, or its copolymer in order to make ion exchange nature grains anchor. Although low density polyethylene, high density polyethylene, the polybutene 1, etc. are mentioned and an ethylene-vinyl alcohol copolymer is mentioned as the polymer which has adhesion ability with wet heat, or its copolymer as the polymer which has adhesion ability with dry heat, or its copolymer, Considering adhesion breaking tenacity with ion exchange nature grains, high density polyethylene or an ethylene-vinyl alcohol copolymer

is preferred, High density polyethylene/polypropylene, the high density polyethylene/poly (4-methylpentene-1) 1, the concentric circle sheath-core type bicomponent fiber that used as the sheath component the component which has the adhesion ability which consists of combination of an ethylene-vinyl alcohol copolymer / polypropylene, or especially an assembled-die bicomponent fiber is preferred.

[0011]And as for the textiles which consist of a component which has said adhesion ability, it is preferred to contain ten to 60weight % in a nonwoven fabric. It is because a mileage becomes large, so the permeability as a separator will be small and the internal pressure inside a cell will rise, if breaking tenacity becomes weak also as a separator and it exceeds 60 weight %, since adhesion breaking tenacity becomes it low that content is less than 10 weight %.

[0012]In the separator for cells of this invention, ion exchange nature grains anchor by at least some resinous principles of the fiber surface of composition textiles. Anchoring by a resinous principle here is a concept containing what pasted up when the thing beforehand mixed by resin itself or grains carried out melting of the fiber surface in each and/or the state where it condensed. Especially in this invention, it is advantageous the time of nonwoven fabric production, or after nonwoven fabric production to anchor ion exchange nature grains uniformly using the adhesion ability of the textiles which consist of a component which has said adhesion ability in the point of exhibiting the function of ion exchange nature grains.

[0013]The polymer system ion exchange resin which consists of cation exchange resin of a styrene system or acrylic, or anion exchange resin of a styrene system or acrylic as said ion exchange nature grain, Or although the inorganic system ion exchange nature grains which consist of that etc. into which titanium oxide, aluminium oxide, zirconium oxide, phosphoric acid zirconiums, these sulfonic groups, or a carboxylic acid group was introduced are mentioned, Inorganic system ion exchange nature grains are preferred in respect of alkali resistance and a heat-resisting property. The zirconium system grains which carried out sulfonation treatment of zirconium oxide or the phosphoric acid zirconium, and introduced the sulfonic group especially are preferred at especially a point excellent in electrolyte holdout.

[0014]And it is preferred that it is less than 30 micrometers, and when mixing and carrying out spinning of the mean particle diameter of said ion exchange nature grain to resin, less than 5 micrometers is preferred [ the mean particle diameter ] in respect of stringiness or exposure nature to a fiber surface of grains. When making it anchor directly by a fiber web or nonwoven-fabric-state voice, and an average pore size of D and a nonwoven fabric is set to Pave and the minimum aperture is set to Pmin for mean particle diameter of ion exchange nature grains, it is preferred that ion exchange nature grains fill a relation of  $P_{min} \leq D \leq P_{ave}$ . If grains cannot support a nonwoven fabric, but pass and exceed Pave when grains are stuck to a nonwoven fabric with an ion exchange nature grain mixed water solution as the mean

particle diameter  $D$  of ion exchange nature grains is less than  $P_{min}$ , It is because a hole of a nonwoven fabric will be blockaded by grains and permeability of a nonwoven fabric will fall. [0015]As for said ion exchange nature grain, it is preferred to anchor two to 60weight % in a nonwoven fabric. It is 10 to 30 weight % more preferably. It is because permeability of a nonwoven fabric will fall if ion exchange capacity and hydrophilicity of a separator fall that content of ion exchange nature grains is less than 2 weight %, a capacity maintenance rate and a core life fall and it exceeds 60 weight %, so internal pressure inside a cell will rise and a battery life will fall.

[0016]Next, a manufacturing method of a separator for cells of this invention is explained. First, spinning of the ion exchange nature grains is mixed and carried out to resin, and if it is a case where it anchors to the textiles themselves beforehand, it will be made to mix using publicly known mixing equipment. For example, it is convenient, when it mixes by Henschel mixer, a super mixer, etc., melting mixing is carried out with publicly known monopodium or a biaxial extruder and it masterbatch-izes beforehand. And using a publicly known melt spinning machine, melt spinning is carried out and a spinning filament of predetermined fineness is produced. A spinning filament is extended if needed and may make textiles treatment adhere. If textiles treatment of hydrophilicity is made to adhere, since initial hydrophilicity will improve further, it is desirable. And if needed, crimp can be given with a crimp grant device and textiles which were cut by predetermined length and anchored ion exchange nature resin to a fiber surface can be obtained. And obtained textiles are nonwoven-fabric-ized by a publicly known nonwoven fabric manufacturing method, and can obtain easily a nonwoven fabric in which ion exchange nature grains anchored.

[0017]On the other hand, if it is a case where it is made to anchor directly by a fiber web or nonwoven-fabric-state voice, a fiber web which makes composition textiles one kind or two kinds or more of polyolefin fibers will be produced. A continuous glass fiber web obtained according to direct method, such as a dry type web which acquired a form of a fiber web by the curd method, the air lei method, etc., a wet web obtained with a wet method or the melt blowing method, and the span bond method, is used. Especially, a wet web which fiber length of said composition textiles becomes from 3-25 mm is preferred at a point of obtaining a homogeneous web. More desirable fiber length is 5-15 mm. Textiles disperse at the time of high-pressure-water style treatment which fiber length mentions later in less than 3 mm, and confounding between textiles becomes insufficient, It is because the dispersibility of textiles in slurry worsens and a uniform nonwoven fabric cannot be undesirably obtained on a process, when manufacturing a nonwoven fabric by a wet paper-making method especially if it exceeds 25 mm.

[0018]These fiber webs are processed by methods, such as heat calender treatment, hot blast processing treatment, and high-pressure-water style treatment. It is convenient when an

assembled-die bicomponent fiber is contained especially in composition textiles, and an assembled-die bicomponent fiber is made to divide, while composition textiles make it interlace by high-pressure-water style treatment.

[0019]Although the metsuke of the obtained nonwoven fabric can be adjusted with the quantity of textiles, it is desirable to use  $30\text{--}100\text{g} / \text{m}^2$ . It is because the breaking tenacity of a nonwoven fabric becomes low, so gas permeability etc. will fall by less than  $30\text{g} / \text{m}^2$  if it becomes easy to generate short-circuit between a positive electrode and a negative electrode and  $100\text{g} / \text{m}^2$  is exceeded.

[0020]And the thing used as the grain mixed solution which was made to distribute ion exchange nature grains in an aqueous solution, and was mixed, Or impregnate, sprinkle or apply a powdered thing to the fiber web or nonwoven fabric which was able to be obtained by a publicly known method, use dry heat or wet heat after that, ion exchange nature grains are made to anchor by at least some resinous principles of the fiber surface of composition textiles, and it makes with the separator for cells. After sprinkling or applying ion exchange nature grains between a two-layer fiber web or a nonwoven fabric at least at this time, it may be made to anchor with dry heat or wet heat. Other sheets, such as a nonwoven fabric and a film, may be laminated at least on one side of the nonwoven fabric to which ion exchange nature grains were stuck. [ and the conditions pasted up by at least some resinous principles ] For example, if it is high density polyethylene, it is good for a hot blast, a hot calender roll, etc. of temperature near  $120\text{--}140^\circ\text{C}$  to let pass and carry out dry heat adhesion, and if it is an ethylene-vinyl alcohol copolymer, it is good for a hot blast, a hot calender roll, etc. of not less than  $70^\circ\text{C}$  to carry out wet heat adhesion through the fiber web of a moisture state. Of course, control of gauge by the hydrophilization treatment and calender treatment of others, such as grant of a hydrophilic surfactant and a corona, may be performed if needed.

[0021]Thus, a cell incorporating an obtained separator for cells has low internal pressure, and becomes the thing excellent in battery characteristics, such as a core life and a capacity maintenance rate.

[0022]

[Working example]Hereafter, an embodiment is given and the contents of this invention are explained concretely. An obtained nonwoven fabric aperture, permeability, an electrolyte holding rate, ion exchange capacity, internal pressure, a core life, and a capacity maintenance rate were measured as follows.

[0023](1) It measured according to nonwoven fabric aperture ASTM F316-86 (the bubble point method).

[0024](2) It measured according to permeability JIS L 1096.

[0025](3) Measure weight (W) of electrolyte holding rate \*\*\*\* and a moisture equilibrium state of a specimen to 1 mg. Next, after immersing a specimen into a KOH solution of specific

gravity 1.30, making a KOH solution absorb for 1 hour, pulling up out of liquid and neglecting it for 10 minutes, weight ( $W_1$ ) of a specimen was measured and an electrolyte holding rate was computed from a formula of electrolyte holding rate (%) =  $(W_1 - W) / (W) \times 100$ .

[0026](4) Make ion-exchange-capacity \*\*\*\* and a specimen immersed into 1M hydrochloric acid for 2 hours. The specimen is washed until it becomes neutrality with distilled water, and it dries at 100 \*\*. A specimen after the desiccation is put into a beaker, and 10 ml of 0.1M potassium hydroxide is added into it. 10 ml of potassium hydroxide is put into another beaker. The standard titration of the potassium hydroxide of both beaker of these is carried out with 0.1M hydrochloric acid using a phenolphthalein indicator. Thus, measured ion exchange capacity is computed by a following formula.

As for titer from a beaker into which, as for =  $[IEC] (t_2 - t_1) / 10W_1 t_1$ , a specimen went, titer from a beaker in which a specimen is not  $[t_2]$  contained, and  $W_1$ , weight of a specimen is shown.

[0027](5) A cylindrical shape sealing nickel-hydrogen battery negative electrode added and kneaded water to a hydrogen storing metal alloy, carbonyl nickel, carboxymethylcellulose (CMC), and polytetrafluoroethylene (PTFE), and adjusted slurry. After carrying out the immersion coating of this slurry at a punching metal which carried out the nickel plate, pressurization molding was dried and carried out at 80 \*\*, and a hydrogen storing metal alloy negative electrode was created. A publicly known sintering type nickel pole was used for a positive electrode. A cylindrical shape sealing nickel-hydrogen battery was produced by intercalating in a battery can on both sides of each separator, and pouring in an electrolyte between the above-mentioned negative electrode and a positive electrode.

[0028](6) Assemble a cell which made a hole in a bottom of an internal pressure battery can, and attached a pressure sensor. After using this cell and performing initial activity, at a rate of charge 0.1C, it was considered as the final voltage 1.0V at a rate of discharge 0.1C, and 5 cycle charge and discharge were repeated for relaxation time 0.5 hour for 16 hours. Then, a pressure after charging at a rate of 1.0C for 120 minutes was measured.

[0029](7) A nickel-hydrogen battery which carried out the core life aforementioned production was made into the final voltage 1.0V at a rate of discharge 0.1C with a rate of charge 0.1C for pause 0.5 hour for 12 hours, 10 cycle charge and discharge were repeated, and cell initial activity was performed. And it asked for a number of cycles when a capacity factor over theoretical capacity became 90% or less with a rate (final voltage 1.0V) of discharge 1.0C at a rate of charge 1.0C for relaxation time 0.5 hour for 1.2 hours, after performing initial activity. Charge and discharge were performed at 25 \*\*.

[0030]After performing capacity maintenance rate initial activity, at the rate of charge 0.1C (8) 12 hours, It was considered as the final voltage 1.0V at the rate of discharge 0.1C, and the

ratio of remaining capacity (rate discharge of 0.1C, final voltage 1.0V) when it is neglected for 14 days under 45 °C after charge on the conditions (rate of 0.1C) was made into the capacity maintenance rate after self-discharge to the discharge capacity after 5 cycle \*\*\*\*\* for pause 0.5 hour. Charge and discharge were performed at 25 °C.

[0031][Embodiment 1] Fineness 1.6dtex which high density polyethylene and a core component become from polypropylene in a sheath component, 6 mm of fiber length's sheath-core type bicomponent fiber (henceforth A textiles) 30 weight %, Fineness 3.3dtex by which the textiles section which consists of combination of polypropylene / ethylene-vinyl alcohol copolymer was radiately divided into 16, 5 mm of fiber length's assembled-die bicomponent fiber (henceforth B textiles) 50 weight %, And wet paper making of 20 weight % was carried out for fineness 1.1dtex and 6 mm of fiber length's polypropylene fiber (henceforth C textiles), the wet nonwoven fabric was produced, injected the high-pressure pillar-shaped stream of hydraulic pressure 10MPa, B textiles were made to divide, and the base fabric for ion exchange nature grain anchoring was produced. The metsukes of this base fabric were 50g / m<sup>2</sup>, the minimum aperture Pmin was 5.5 micrometers and the average pore size Pave was 32 micrometers.

[0032]Next, the ion exchange nature grains (the product made from the first Rare element Chemicals and the following call  $ZrO_2/SO_4$ ) and water which carried out sulfonation treatment of the zirconium oxide whose mean particle diameter D is 10 micrometers are mixed, and a mixed water solution is produced 50weight %. And a mixed solution is sprayed on said base fabric at ordinary temperature. Then, while carrying out wet heat adhesion of the grains mainly with the ethylene-vinyl alcohol copolymer among composition textiles at 135 °C, it was made to dry, and the separator for cells was obtained.

[0033][Embodiment 2] The separator for cells was obtained by the same method as Embodiment 1 except spraying the mixed water solution whose amount of  $ZrO_2/SO_4$  is 20 weight % on a base fabric.

[0034][Embodiment 3] The separator for cells was obtained by the same method as Embodiment 1 except spraying the mixed water solution whose amount of  $ZrO_2/SO_4$  is 75 weight % on a nonwoven fabric.

[0035][Embodiment 4] Wet paper making of 60 weight % of A textiles and 40 weight % of the C textiles was carried out, and the base fabric for ion exchange nature grain anchoring was produced. The metsukes of this base fabric were 60g / m<sup>2</sup>, the minimum aperture Pmin was 20 micrometers and the average pore size Pave was 150 micrometers. Next, after spraying the mixed solution of Embodiment 1 at ordinary temperature, while carrying out heat-of-fusion adhesion of the grains mainly with polyethylene among composition textiles at 140 °C, it was made to dry, and the separator for cells was obtained.



[0036][Comparative example 1] The separator for cells was obtained by the same method as Embodiment 1 except not spraying  $\text{ZrO}_2/\text{SO}_4$ .

[0037][Comparative example 2] Wet paper making of 60 weight % of A textiles and 40 weight % of the C textiles was carried out, and the wet nonwoven fabric was produced. And the separator for cells which the toluene solution of  $\text{ZrO}_2/\text{SO}_4$  and a styrene ethylene-butylene-styrene system copolymer (SEBS) was impregnated with, dried the obtained nonwoven fabric, and anchored  $\text{ZrO}_2/\text{SO}_4$  to the nonwoven fabric by SEBS resin was obtained. The physical properties of Embodiments 1-4 and the comparative examples 1-2 are shown in Table 1.

[0038]

[Table 1]

	実施例				比較例	
	1	2	3	4	1	2
粒子固着量(重量%)	31	10	70	15	0	28
通気度(ccs)	19	21	3	23	22	5
保液率(%)	411	378	433	341	224	198
イオン交換容量(meq/g)	1.8	1.5	2.0	1.6	0	1.7
内圧(kg/cm <sup>2</sup> )	6	5	12	5	5	4
サイクル寿命(cycle)	451	445	227	392	201	314
容量維持率(%)	80	79	81	78	53	81
生産性	○	○	○	○	◎	×

[0039]Especially in Embodiments 1 and 2, the advanced core life and the capacity maintenance rate were obtained among the separators for cells of Embodiments 1-4. In the comparative example 1, since ion exchange nature grains did not exist, there was no ion exchange capacity, the electrolyte holding rate also became low, and the core life and the capacity maintenance rate became low. In the comparative example 2, since ion exchange nature grains were fixed by SEBS resin, SEBS resin made the hole of the nonwoven fabric blockade to some extent, the permeability of the nonwoven fabric fell, the internal pressure inside a cell rose, and the core life became low.

[0040]

[Effect of the Invention][ by the separator for cells of this invention being a nonwoven fabric which makes composition textiles one kind or two kinds or more of polyolefin fibers, and

making ion exchange nature grains anchor by at least some resinous principles of the fiber surface of composition textiles ] Since resin for adhesion is not needed specially, the opening between composition textiles can be secured and the separator for cells excellent in the solution retention of an electrolyte is obtained. In anchoring to the nonwoven fabric of ion exchange nature grains, in order not to use an organic solvent, textiles breaking tenacity does not decline and the breaking tenacity of a separator not only does not decline, but it excels in productivity.

[0041]The ion exchange nature grains used for the separator for cells of this invention are excellent in especially electrolyte holdout by carrying out sulfonation treatment of zirconium oxide or the phosphoric acid zirconium, and introducing a sulfonic group. And the cell incorporating the separator for cells of this invention has low internal pressure, and is suitable for the alkaline batteries excellent in battery characteristics, such as a core life and a capacity maintenance rate, such as a nickel cadmium battery, a nickel zinc carbon cell, and a nickel-hydrogen battery.

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[Translation done.]